

SUBSTITUTE SPECIFICATION**PULTRUSION PRODUCTS OF GLASS-FIBER PHENOLIC RESINS****SPECIFICATION****FIELD OF THE INVENTION**

The present invention relates to a manufactured product  
5 made from phenolic resin obtained by pultrusion, and to the  
process for making it.

**BACKGROUND OF THE INVENTION**

For some time manufactured products obtained by  
pultrusion and made from composite material of glass fibers in a  
10 phenolic-resin-based matrix have been known.

One of the drawbacks common to many composite  
materials, and especially for those composite materials having a  
phenolic-resin-based matrix, derives from the retraction of the  
matrix during polymerization in the mold, which generates in the  
15 resulting manufactured product substantial surface microporosity  
and substantial surface roughness and consequently a fiber phase  
located close to the outer surface of the protruded manufactured  
product. The surface microporosity of the manufactured product  
thus promotes the degrading action of ultraviolet rays with the  
20 result that the manufactured product is subjected to a  
progressive deterioration which penalizes its performance until  
it is quickly rendered unusable.

The surface microporosity of the manufactured product also generates non-negligible friction between the manufactured product and the extrusion mold with the result that the latter is subjected to continuous and inexorable wear. To at least partially avoid these drawbacks a very fine glass fiber is used that is able to attenuate the surface roughness or the surface projection of the fibers on the manufactured product. However, the use of this type of very fine glass fibre has an enormous impact upon the cost of the end manufactured product.

For this reason, in place of the very fine glass fiber, a larger and therefore considerably more cost effective glass fiber is used. However, in this case the use of a larger, glass fiber requires that the resin matrix be additived with a loading able to attenuate the surface porosity of the manufactured product.

#### OBJECTS OF THE INVENTION

An object of the present invention is, therefore, that of making a manufactured product by pultrusion in a glass fiber composite with phenolic resin matrix which allows the aforementioned technical drawbacks of the prior art to be eliminated.

Another object is to provide a manufactured product which eliminates the drawbacks due to the shrinking of the phenolic resin during cross-linking.

Another purpose is to provide a manufactured product by pultrusion which does not display surface microporosity or projection of the fibers.

It is also an object to provide a manufactured product that is highly resistant to the degrading action of ultraviolet rays.

A further object is to provide a manufactured product with high fireproof capability.

Still another object is to provide a manufactured product which does not cause the progressive deterioration by wear of the extrusion mold in which it is generated.

It is also an object to provide a manufactured product having suitable mechanical and/or chemical and/or physical and/or electrical and/or thermal surface properties which can condition its suitability for uses for which it is intended.

Yet a further object is to provide a manufactured product by pultrusion that is cost-effective through a simple production process.

#### SUMMARY OF THE INVENTION

These and other objects of the present invention are accomplished with a manufactured product obtained by pultrusion and made from composite material of natural and/or synthetic fibers in a phenolic-resin-based matrix, at least one portion of which has a cellulose-based coating.

Preferably the fibers are glass fibers. In particular, the phenolic resin intimately impregnates the cellulose fibers, then in the cross-linking process it reacts with the active hydroxy groups of the cellulose, generating a homogeneous product capable of carrying out an effective fireproof action.

The present invention also includes a pultrusion process for producing a manufactured product of a composite in synthetic and/or natural fibers with a phenolic-resin-based matrix, which comprises the following steps:

feeding continuous synthetic and/or natural fibers in a phenolic resin bath for the impregnation of said fibers;

associating a coating of cellulose-based material with at least one portion of at least one of the most outer fibers;

compacting the composite thus coated;

shaping and/or sizing the compacted composite and carrying out the finishing of the shaped and/or sized composite.

The coating can be associated with the fibers upstream, downstream or inside the phenolic resin bath and the fibers can also be preimpregnated with phenolic resin upstream of the impregnation bath.

The coating can advantageously be associated with a mat of continuous fibers before the fibers enter the resin bath. Preferably, after the impregnation of the fibers but before compacting, the composite is covered with a protective sheet of material resistant to thermal and mechanical stresses. Such a protective sheet allows the coating in cellulose-based material

to be protected and the resin to be held when the composite is compacted and then shaped. Such a protective sheet is naturally removed at the end of the shaping of the composite.

#### BRIEF DESCRIPTION OF THE DRAWING

5 Further characteristics and advantages of the invention shall become clearer from the description of a preferred but not exclusive embodiment of the manufactured product according to the invention, with reference to the attached drawings, in which:

Figure 1 schematically shows a closed pultrusion mold  
10 for making a manufactured product in accordance with the present finding;

Figure 2 shows a cross section view of a manufactured product in accordance with the present invention; and

Figure 3 schematically shows a further embodiment of a  
15 pultrusion apparatus for making a manufactured product in accordance with the present finding.

#### SPECIFIC DESCRIPTION

In Fig. 1, a pultrusion apparatus 1 is shown with the mold 12 closed. The apparatus 1 comprises a closed controlled  
20 temperature mold 12, preferably heated, having multiple inlet openings for the fibers 14, preferably continuous glass fibers, arranged alternately with multiple inlet openings for the phenolic resin 16.

Of course, the phenolic resin can be pure or loaded according to the application.

Outside of the inlet openings for the outermost bands of fibers 14 at least one inlet opening is provided for a coating foil 15 made from cellulose-based material.

The heated mold preferably contains impregnated projections such as impregnation pins 18 around which the various bands of fibers 14 and the coating layers 15 pass firstly over and then under (or vice-versa) to promote the impregnation by the resin. Moreover, a detection means 20 of the pressure or volume of the resin in the mold is connected with the mold and a system for controlling pressure or volume can also optionally be included as a part of the apparatus.

The mold also has an outlet opening 22 where the bands of fibers and the impregnated coating layers converge. The inlet openings for the fibers 14 and the coating layers 15 and the outlet opening 22 are sized in such a way that the resin cannot flow back through the inlet openings for the fibers 14 and the coating layers 15.

The apparatus preferably comprises a means for compacting the composite, a means for shaping and/or sizing the compacted composite and preferably a second means for controlling the temperature, and a means for finishing the shaped and/or sized composite.

Advantageously, the compacting means, the shaping and/or sizing means and the finishing means can all be in a single and annexed extrusion apparatus.

In the present embodiment the coating layers 15 are associated with the most outer bands of fibers inside the apparatus.

In a different embodiment of the present invention the coating layers 15 are applied to the most outer bands of fibers upstream or downstream of the apparatus 1.

In a further embodiment of the present invention the coating layers 15 are preimpregnated with resin upstream of the apparatus.

With reference to Fig. 3, the pultrusion plant 30 comprises a creel 31 in which the glass fibers 33 are housed and guided to the open impregnation bath generically indicated with 34.

A laminar coating 32 of cellulose-based material that unwinds from a relative reel is associated with the upper band of the mass of fibers unwound from the creel 31, before the entry into the impregnation bath 34.

Inside the impregnation bath or tank 34 there are means for impregnating the mass of glass fiber with phenolic resin. The impregnation means can be defined by impregnation members, not represented, rather than cylinders suitable either for allowing the dipping and divarication of the glass fiber inside the resin,

or else by a bathing roller suitable for taking the resin over the glass fiber during its passage.

The plant is also provided with shaping means defined by a pultrusion mold 35 heated to activate the cross-linking of the matrix of the composite.

The plant also has a pulling mechanism 36 which can consist of a belted trailer or two alternating trucks in order to ensure continuous movement.

Finally, there is the cutting station 37 in which the profile 38 is cut into the desired length.

Now with reference to Fig. 2, the manufactured product 24 resulting from the pultrusion process described above has a pure or loaded phenolic resin-based matrix, and a fibrous phase in long glass fibers.

The coating 15 extends on the whole of the outer surface of the manufactured product 24.

The coating 15 can, however, engage just at least a limited and specified portion of the manufactured product 24.

As can be seen from Fig. 2, due to the microporosity and roughness of the matrix of the manufactured product 24 some peripheral long fibers 14 can have protruding portions. In any case, thanks to the coating 15 these delicate portions of protruding fiber are protected by the action of atmospheric agents and in particular by ultraviolet rays. But this is not all. Thanks to the deep impregnation of the cellulose fibers of the coating 15 with the phenolic resin, the cellulose fibers,



which are generally highly flammable in nature, in this way acquire a high flame-retardant capability.

The coating of the composite material, which as an example has been illustrated above in the form of a full foil, 5 equally advantageously can be in the form of a foil of cellulose-based material equipped with a plurality of through holes, in the form of flakes of cellulose-based material, a powder of cellulose-based material, or else in the form of a network of cellulose-based material.

10 Such a cellulose-based material is preferably paper or card or the like.

Advantageously, at least a portion of the exposed surface of said laminar coating can be made smooth, rough or abrasive or it can be embossed or else it can have many through 15 holes. Of course, in the case in which the coating is smooth, advantageously the production of the manufactured product does not determine the wear of the extrusion mold.

Finally, it can be foreseen that the material of the cellulose-based coating, if in the form of flakes or powder, can 20 be associated with the impregnated fibers before compacting feeding them through a matrix carrying an impression, through which the coating material is to be passed, having the same shape as that which one wishes the coating to take up on the manufactured product.

25 The finding thus conceived is susceptible to numerous modifications and variants, all covered by the inventive

22833

concept; moreover, all of the details can be replaced with technically equivalent elements.